Hot Water Decoded

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A detailed knowledge of the rotation-vibration spectrum of water vapor is required in a wide variety of disciplines, from atmospheric chemistry, observations through Earth's atmosphere, and the search for water-based life, to the modeling of cool oxygen-rich stars. This is because spectroscopy, the analysis of light intensity as a function of frequency, is the only means available for the study of distant objects, and water has ubiquitous presence in the Universe. Every molecule has a unique set of frequencies at which it absorbs light, and the pattern of line positions and line strengths allows precise identification and concentration analyses from afar.

In order to deduce the temperature variation of the line strengths for widely diverse conditions, it is necessary to know the line positions, the intrinsic line strengths, and the initial-state internal energy. The line positions can be determined very accurately from experiment. However, even under optimum conditions, it is only possible to obtain line strengths of moderate accuracy at fixed temperature. Thus theoretical calculations are required in order to decompose the line strength into its temperature-dependent Boltzman factor, which depends on the internal energy and the intrinsic line strength. Previous theoretical work has not been accurate enough to assign the initial states for regions of the spectrum that are congested or that involve highly excited rotation-vibration levels; however, recent work at Ames Research Center (ARC) has resulted in a significantly improved calculation of the opacity of water. These calculations achieved a level of accuracy that far exceeded that of previous work and now enables detailed analysis of the experimental spectrum of water.

A widely used low-temperature database of water lines is the HITRAN database, the 1996 release of which contains 30,117 lines for the most prevalent isotope of water; of these, 1,725 were unassigned. It is possible to associate 30,092 of the lines with the ARC theoretical database, and in the process, 133 lines were reassigned and 831 of the unassigned lines were assigned with a very high degree of confidence.

The ARC theoretical water database has also been used in the simulation of the spectrum of a sunspot. The line positions predicted were sufficiently accurate to assign the dominant water peaks, which is a significant accomplishment given the very high density of lines at these elevated temperatures. Because this requires both accurate line positions and accurate line strengths, the simulation demonstrated the reliability of the ARC theoretical water database for high temperatures.

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